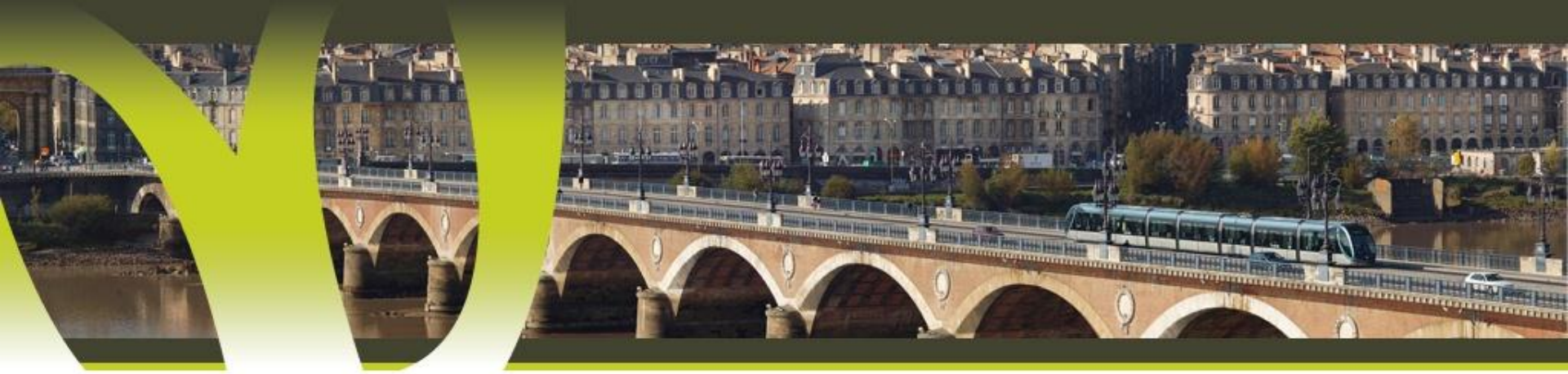


VEGETABLE-BASED BUILDING BLOCKS FOR THE SYNTHESIS OF RENEWABLE POLYURETHANES AND POLYESTERS

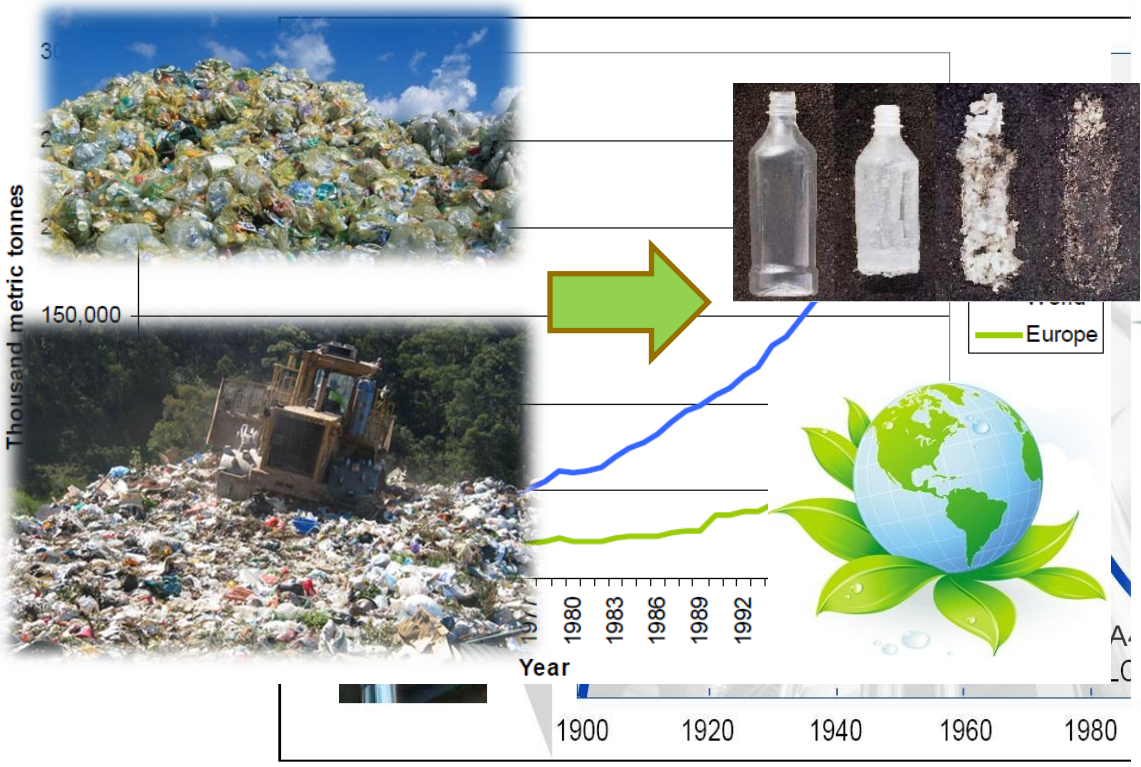
Lise Maisonneuve,[a] Arvind More,[a]
Eric Cloutet,[a] Benoit Gadenne,[b] Carine Alfos,[b] and Henri Cramail [a]

[a] Laboratoire de Chimie des Polymères Organiques, Bordeaux, France
[b] Institut des corps gras (ITERG), Pessac France

ITERG

Fats & Oils expertise

A greener future for polymeric materials



Source : European bioplastics/ Probip 2009

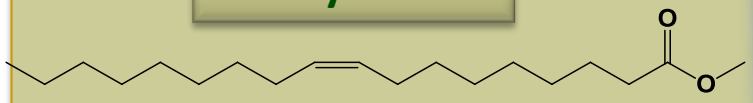
Bio-based raw materials

ITERG

Fats & Oils expertise

Bio-based raw materials

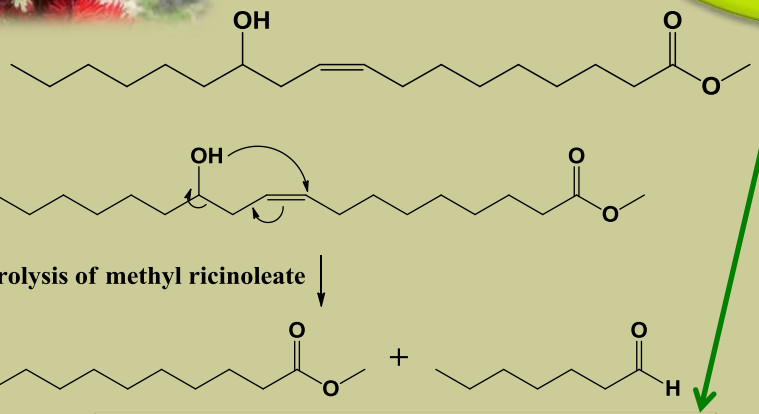
Methyl oleate



~90% in high oleic sunflower oil

Methyl ricinoleate

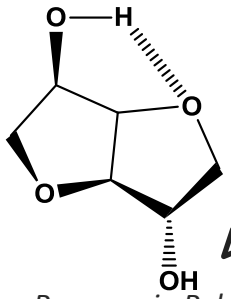
Between 85 and 95% in castor oil



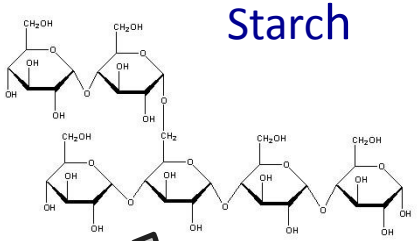
Methyl 10-undecenoate

Journal of the American Oil Chemist Society **1996**, 73(9): 1109-1112.

Isosorbide

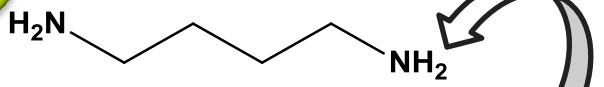


Starch

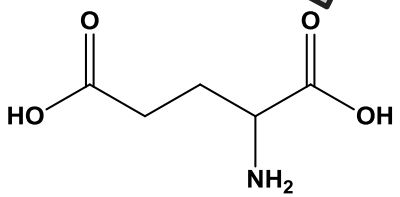


Progress in Polymer Science **2010**, 35(5): 578-622.

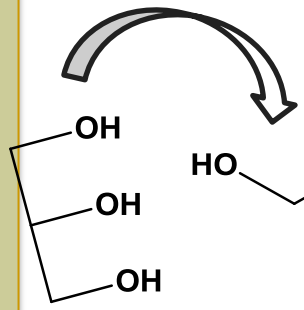
1,4-Diaminobutane



succinic acid

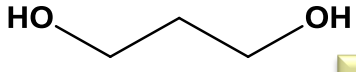


ChemSusChem **2011**, 4(6): 785-791.



Glycerol

1,3-Propanediol

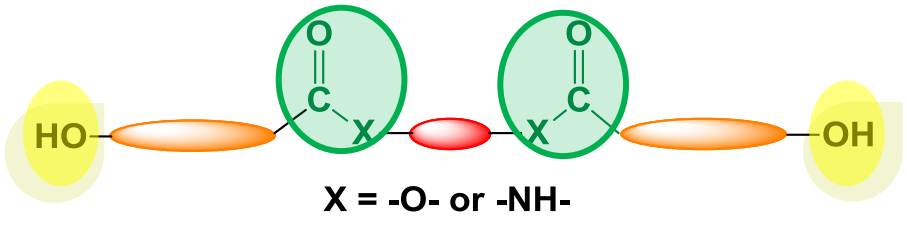


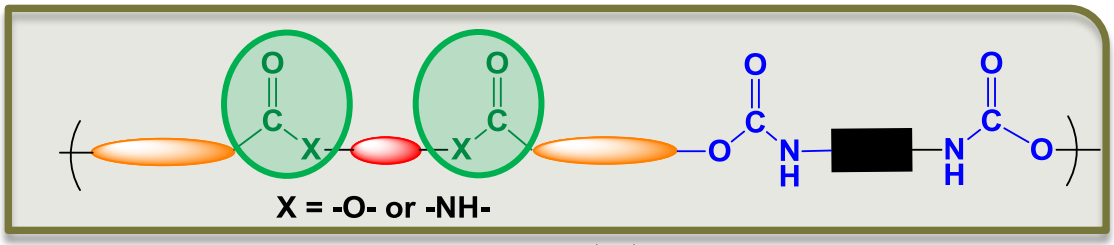
Industrial & Engineering Chemistry Research **2003**, 42(13): 2913-2923.

ITERG

Fats & Oils expertise

Bifunctional building blocks for polyurethanes

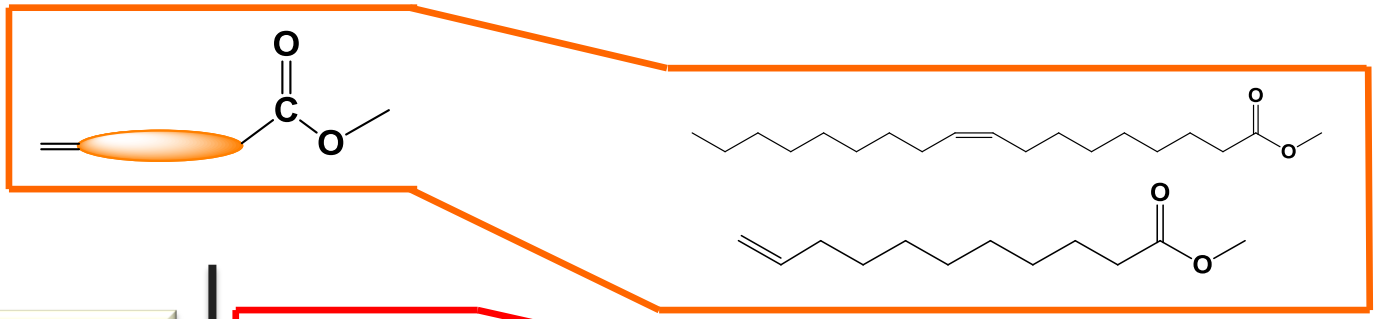




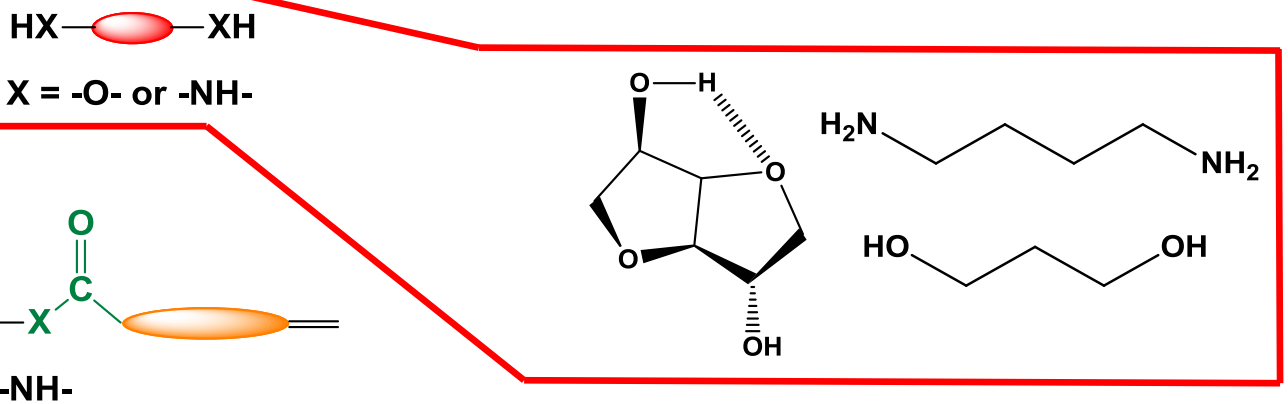
Poly(ester urethane)s
Poly(amide urethane)s
Poly(ester amide urethane)s

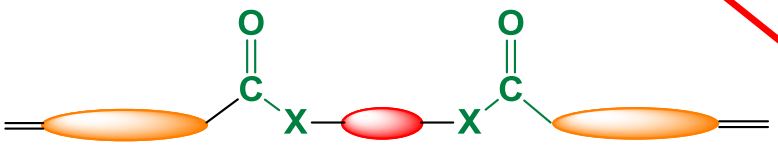
ITERG
Fats & Oils expertise

Synthetic route to the fatty-based diols

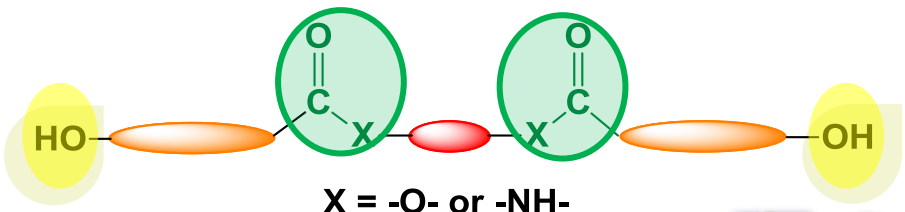


Transesterification and / or Amidation

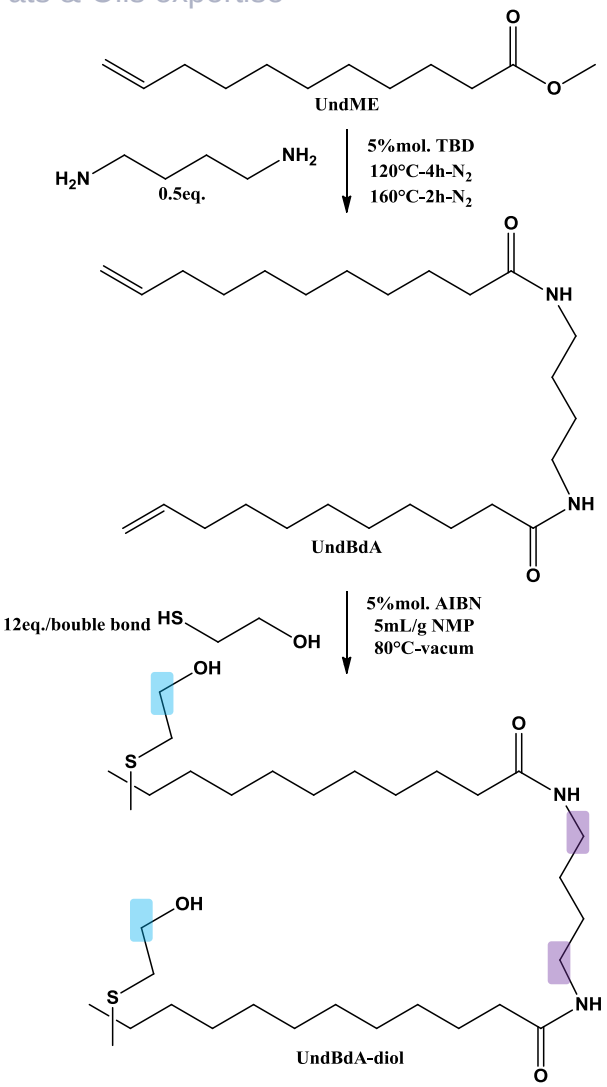


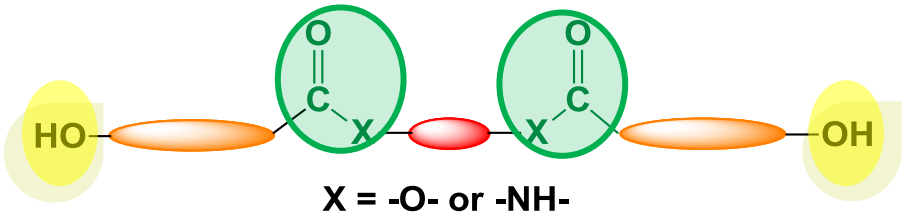


Thiol-ene reaction

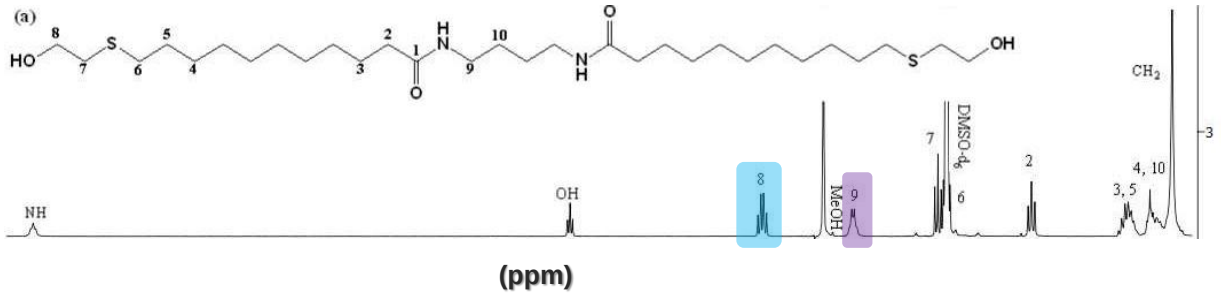


Particular case of diamide diol





Strategy :
Transesterification / Amidation followed by thiol-ene reaction



EP patent 11306491 (**2011**), H. Cramail, L. Maisonneuve, T. Lebarbé, B. Gadenne, C. Alfos, E. Cloutet.

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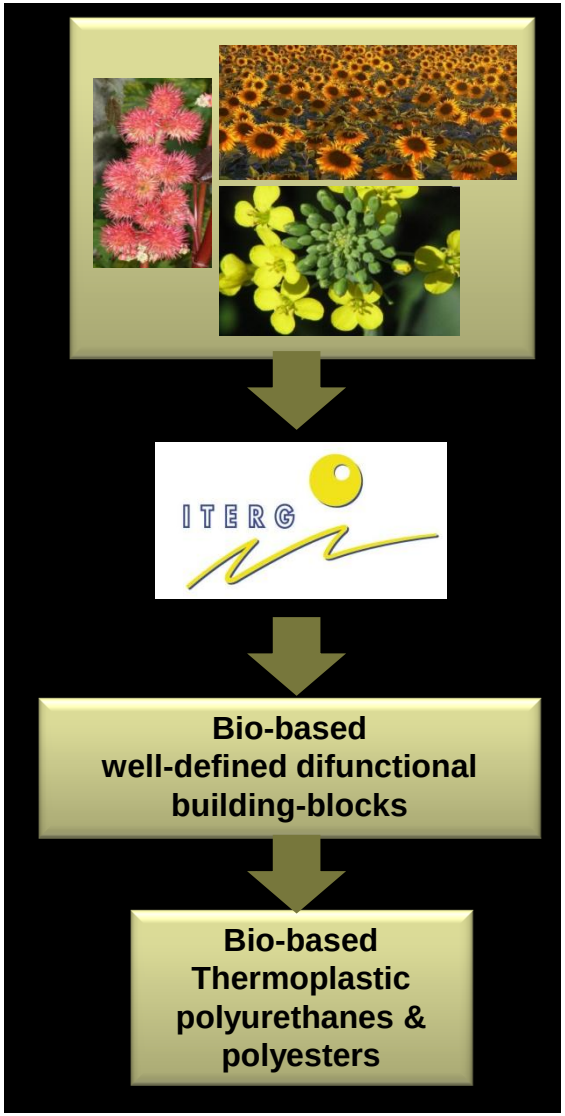
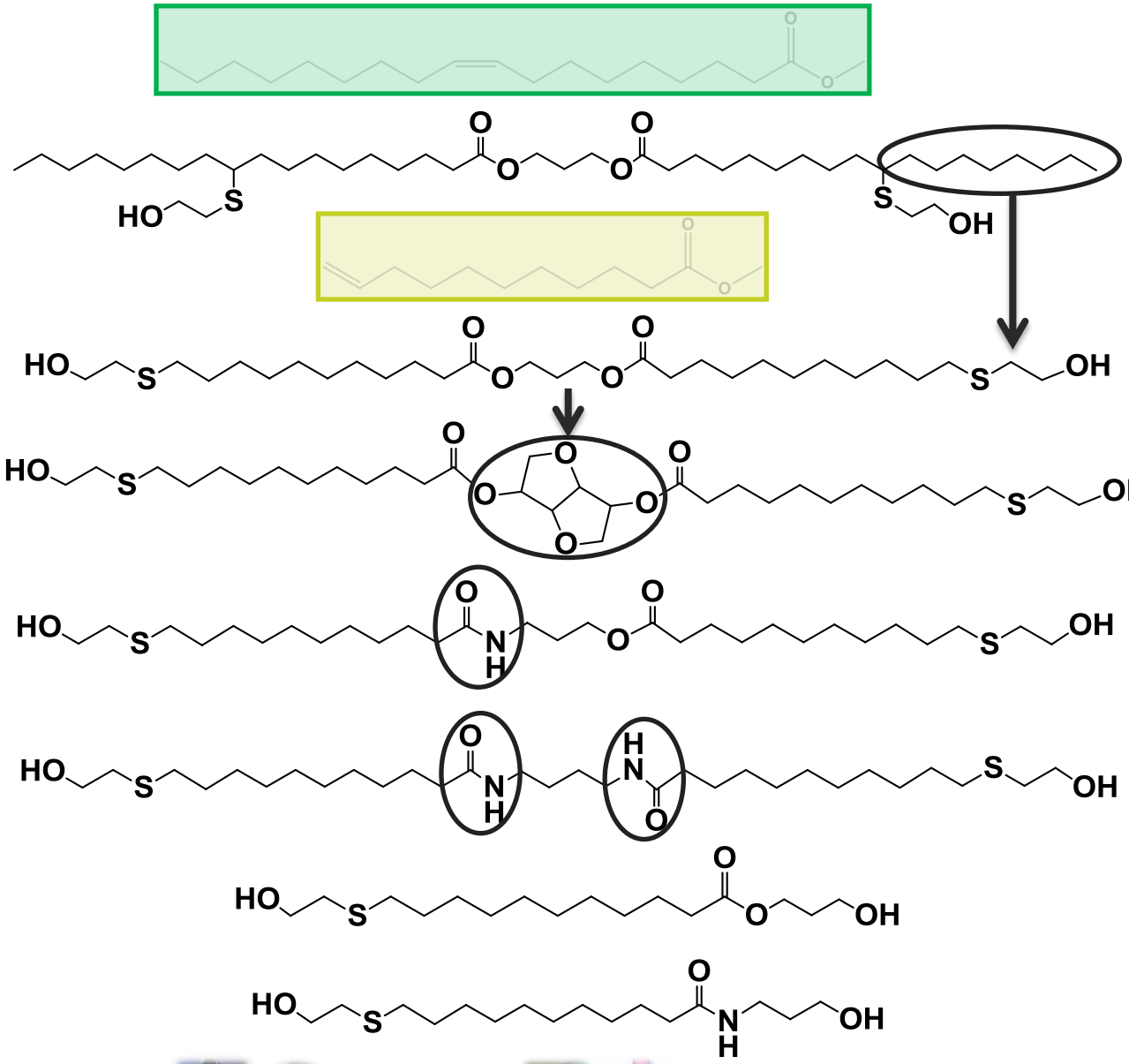
Fats & Oils expertise

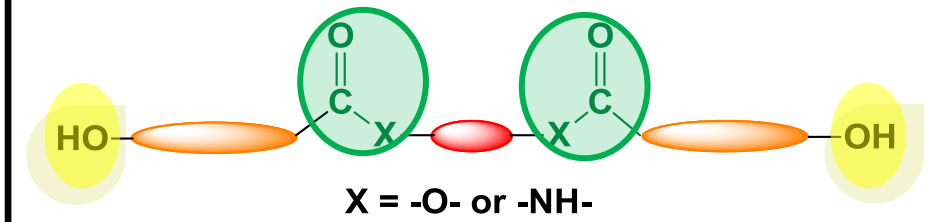
Structure of bio-based diols

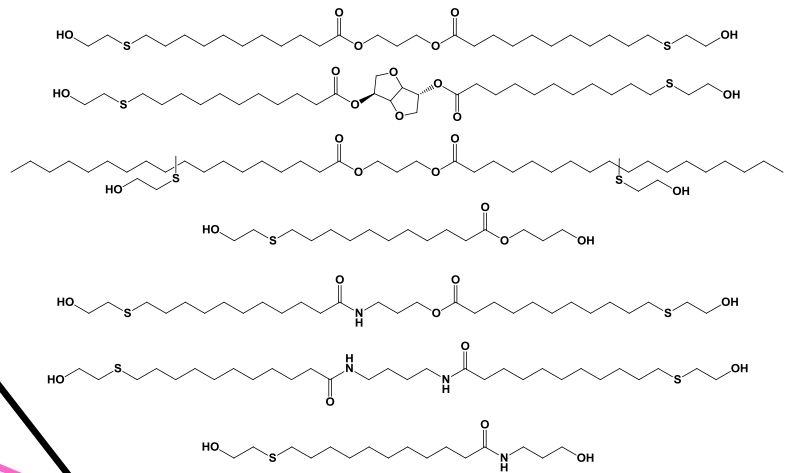


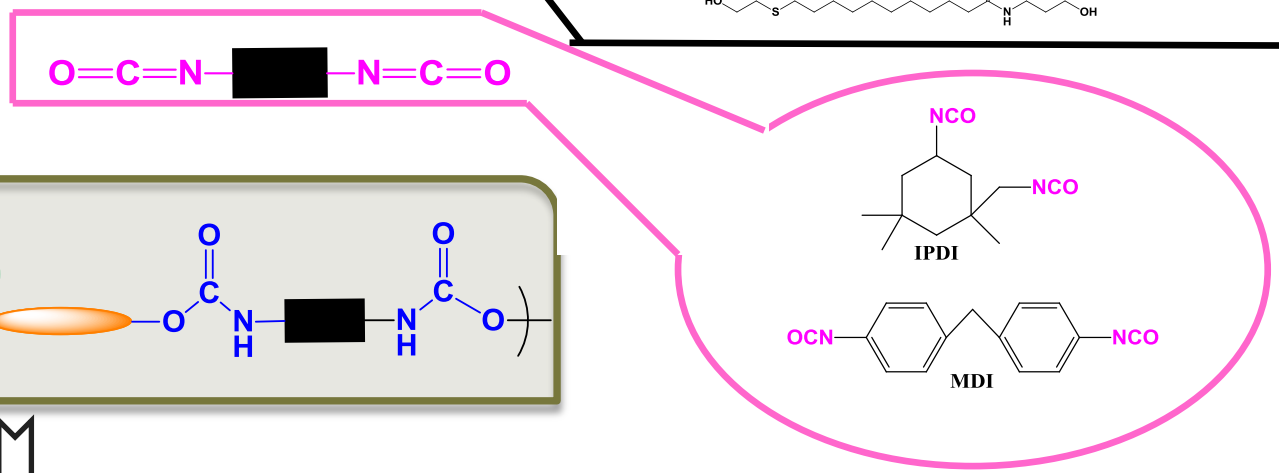


Bifunctional building blocks for polyurethanes

Fats & Oils expertise







Poly(ester urethane)s
Poly(amide urethane)s
Poly(ester amide urethane)s

M_n = 30 000 g.mol^{-1}
M_w = 50 000 g.mol^{-1}
D=1.6

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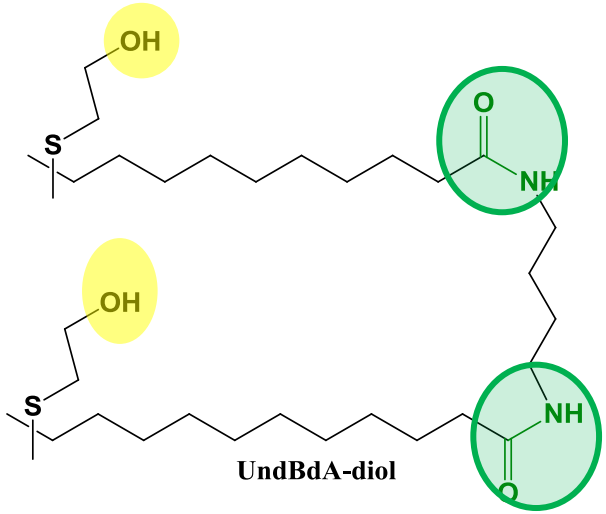
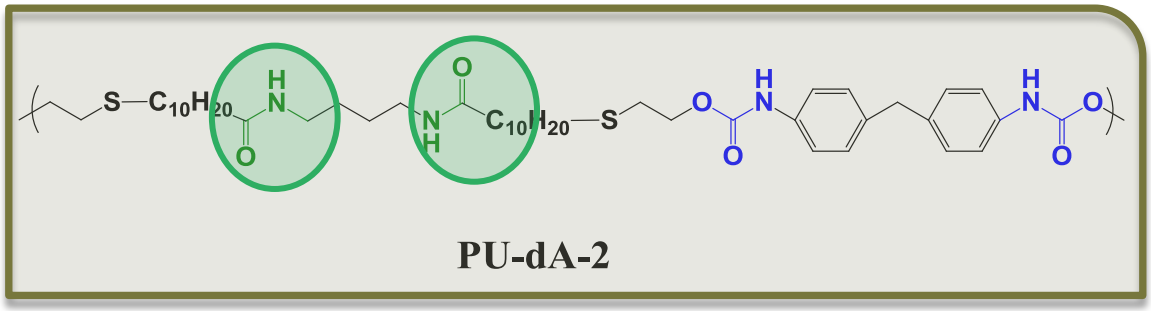
Fats & Oils expertise

Synthetic route to the poly(amide urethane)



0.1wt% DBTDL
80°C
Bulk or DMF
4wt% LiCl (UndBdA-diol)



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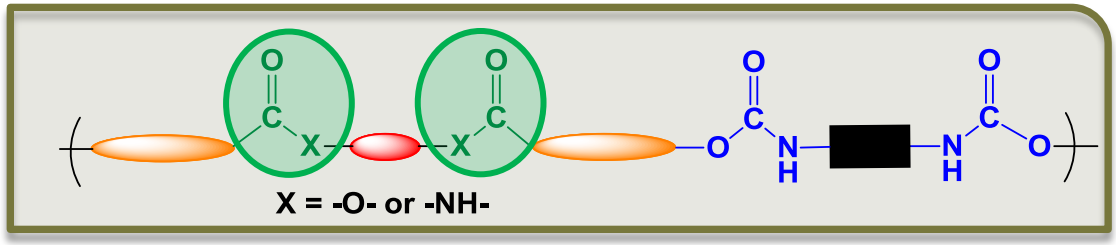
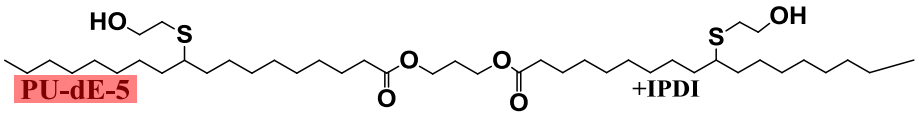
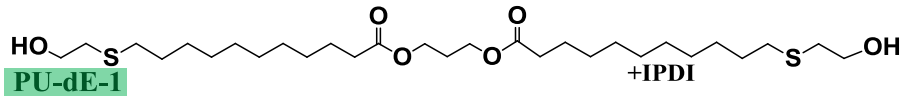
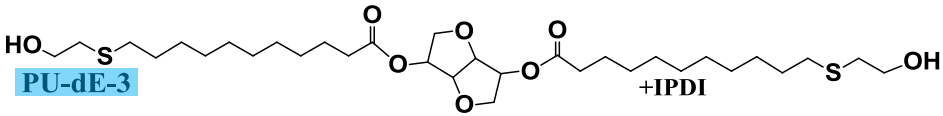
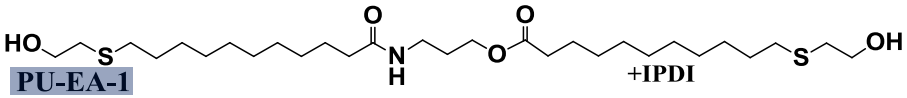
Amorphous polyurethanes

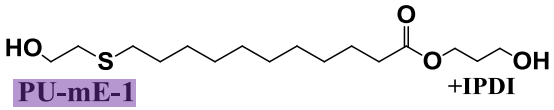


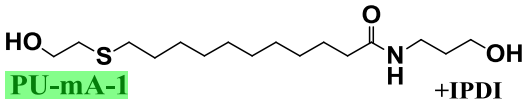


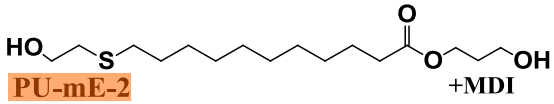


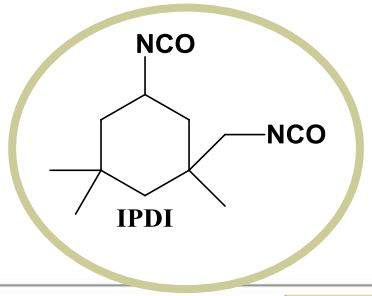


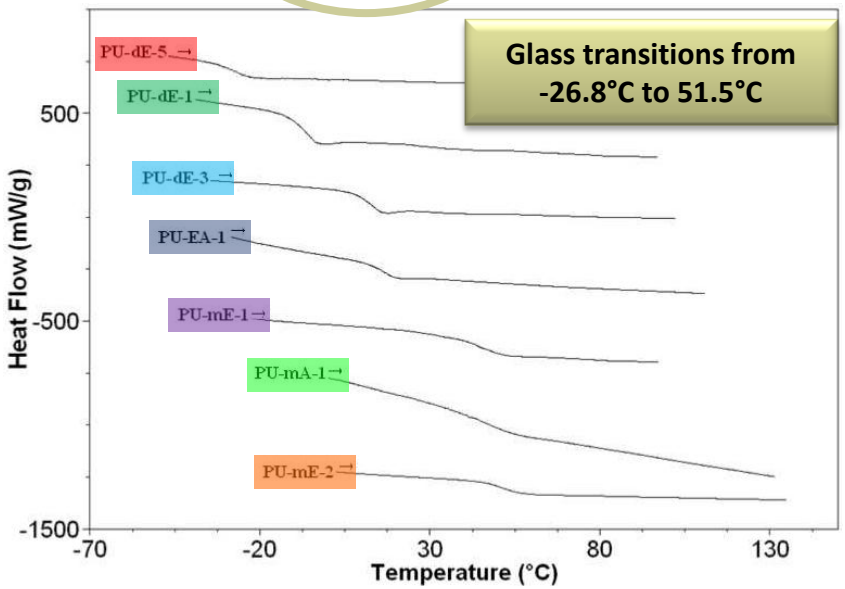






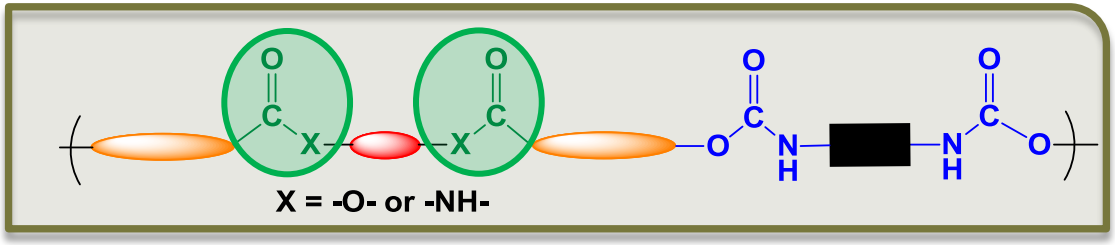


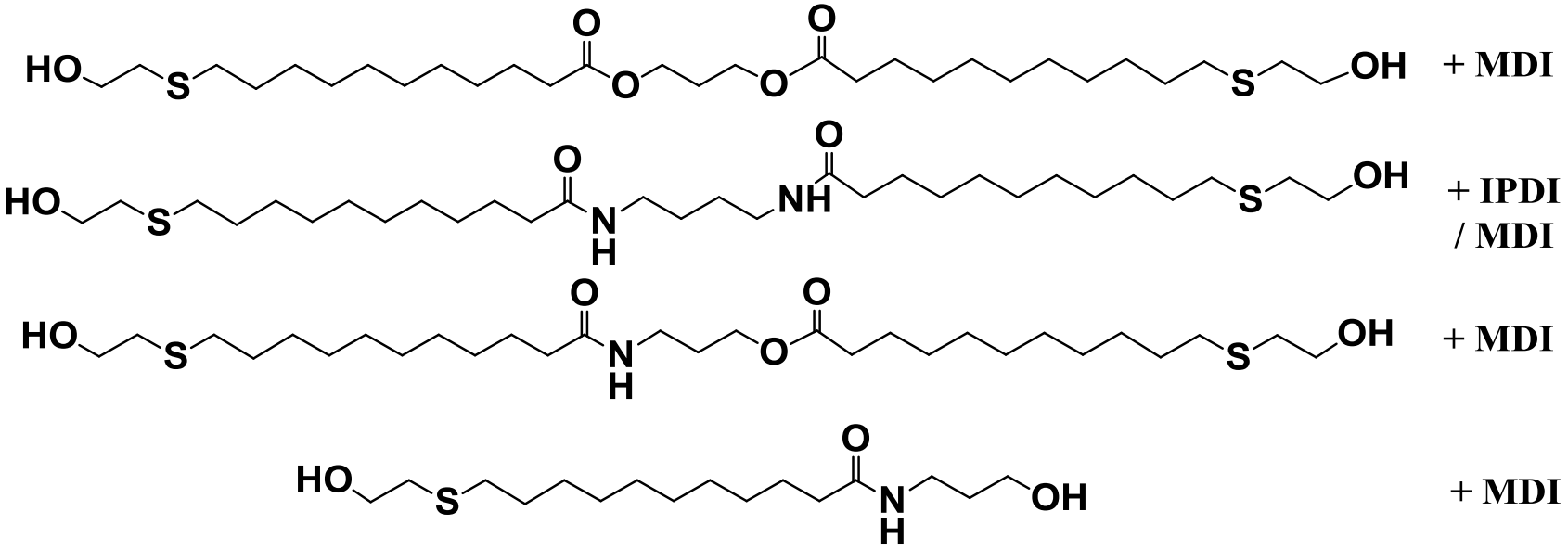




DSC thermograms – Second cycle, 10°C.min^{-1}

Semi-crystalline polyurethanes





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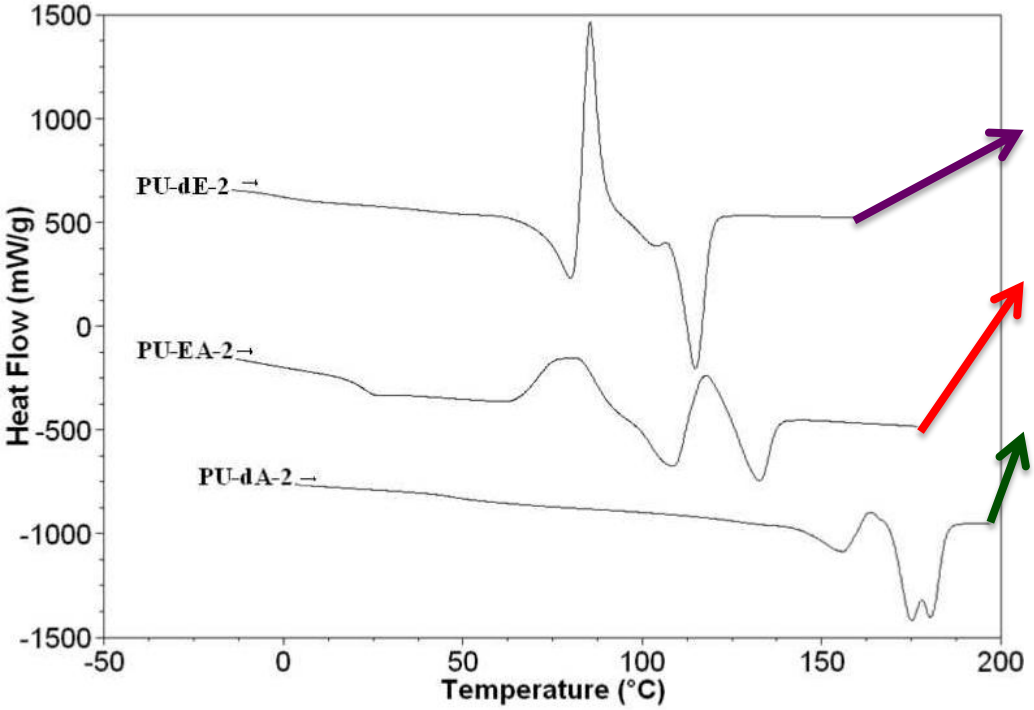
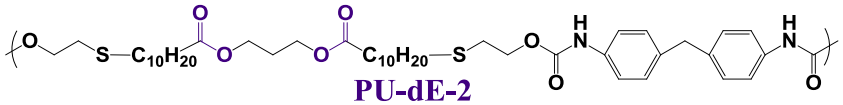
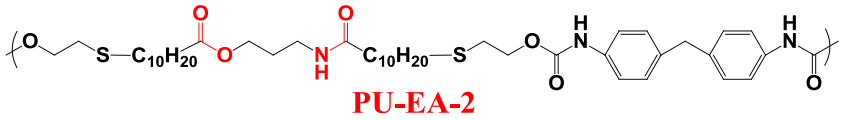
Fats & Oils expertise

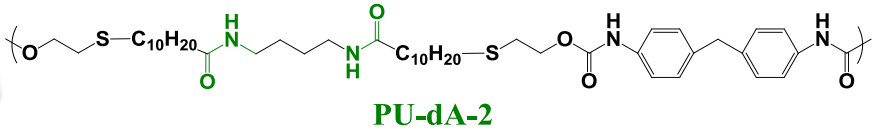
Semi-crystalline polyurethanes



DSC thermograms – Second cycle, 10°C.min^{-1}







Flexibility
High hydrogen bonding

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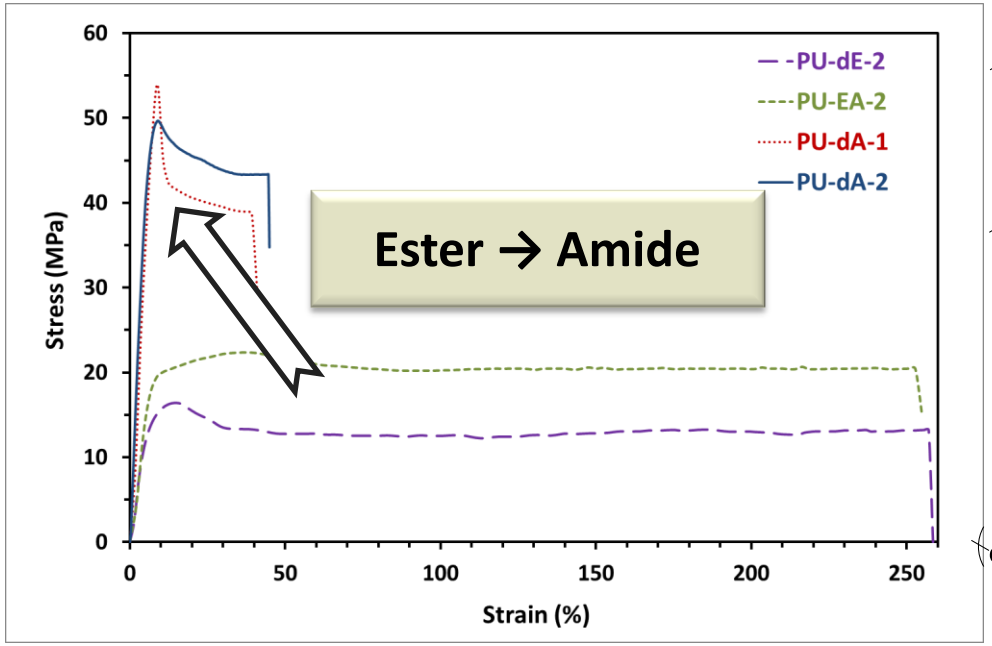
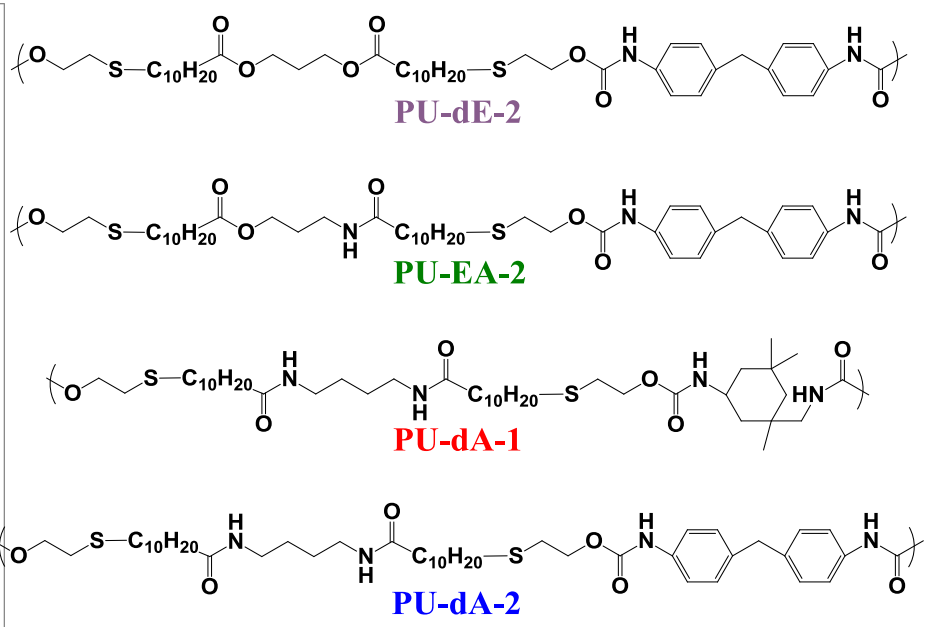
Fats & Oils expertise

Polyurethanes
Mechanical properties via tensile experiments

Samples	Young's modulus (MPa)	Ultimate strength (MPa)	Maximum strain (%)
PU-dE-2	287 ± 35	17.4 ± 2.4	266 ± 24
PU-EA-2	314 ± 33	23.2 ± 1.4	269 ± 26
PU-dA-1	770 ± 68	58.1 ± 3	41 ± 2
PU-dA-2	775 ± 51	48.3 ± 3	44 ± 13





Tensile experiments : Tensile stress versus strain curves

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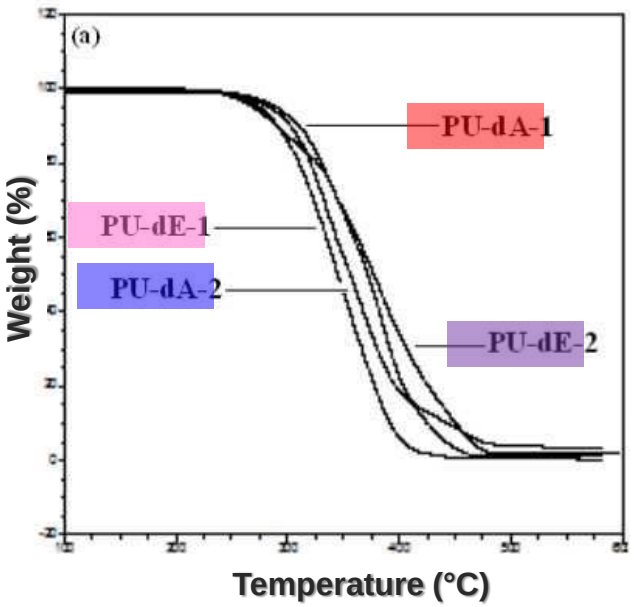
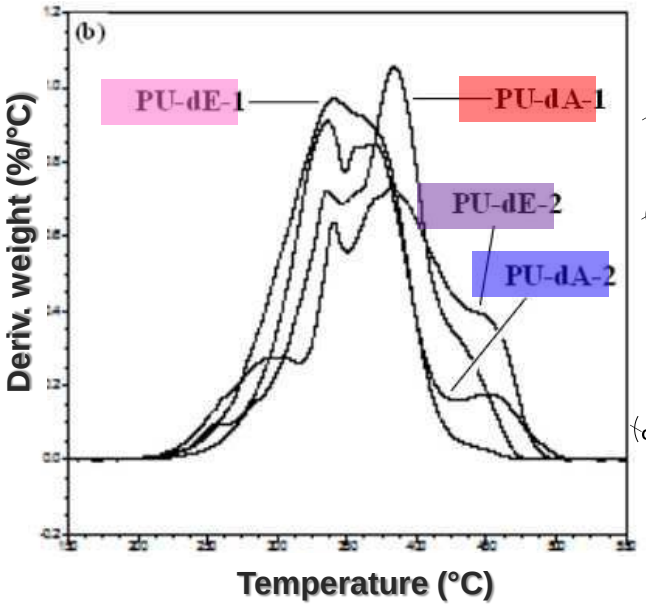
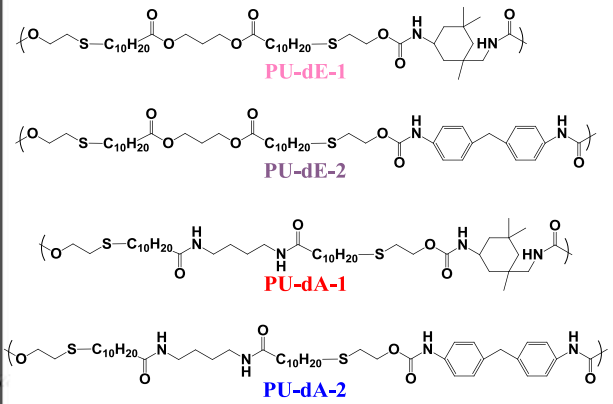
Fats & Oils expertise

2. Poly (ester/amide urethane)s Thermal stability







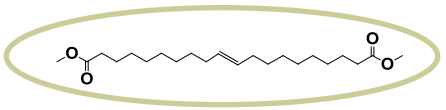
TGA thermograms – N_2, 10°C.min^{-1}

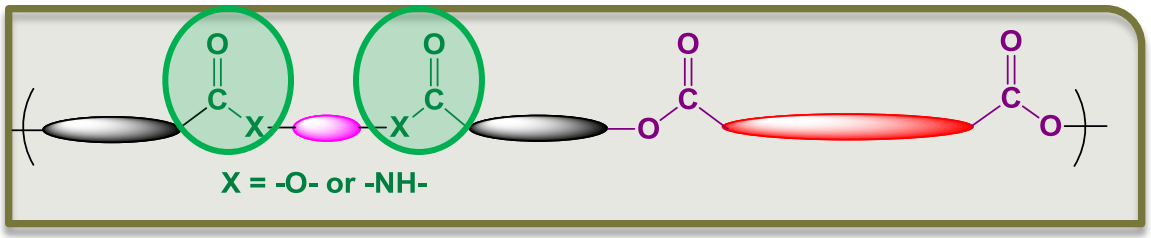
- Typical multiple step degradations behavior
- Urethane functions, thiocarbon chains, ester and amide linkages
- Mostly $T_{5\%}$ > 280°C

ITERG
Fats & Oils expertise

Polyesters : Our strategy to more robust fatty-acid based materials

Castor oil





Polyesters	Poly(ester-amide)s
-biodegradable -Poor thermomechanical properties	-biodegradable -Good thermomechanical properties

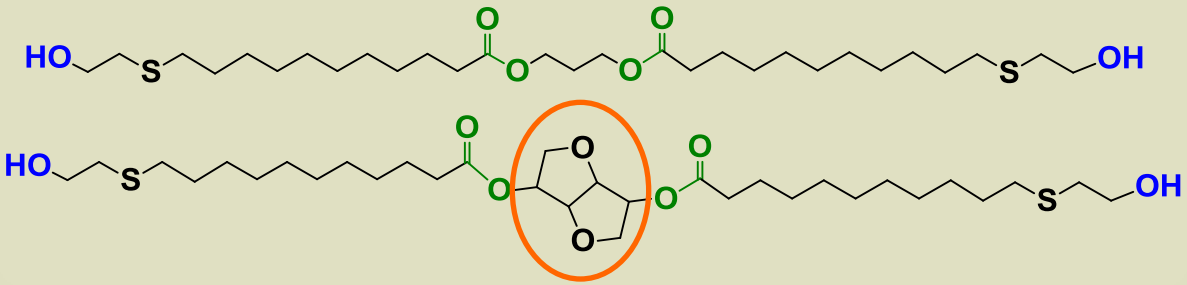
Our strategy to more robust fatty-acid based materials

Fats & Oils expertise

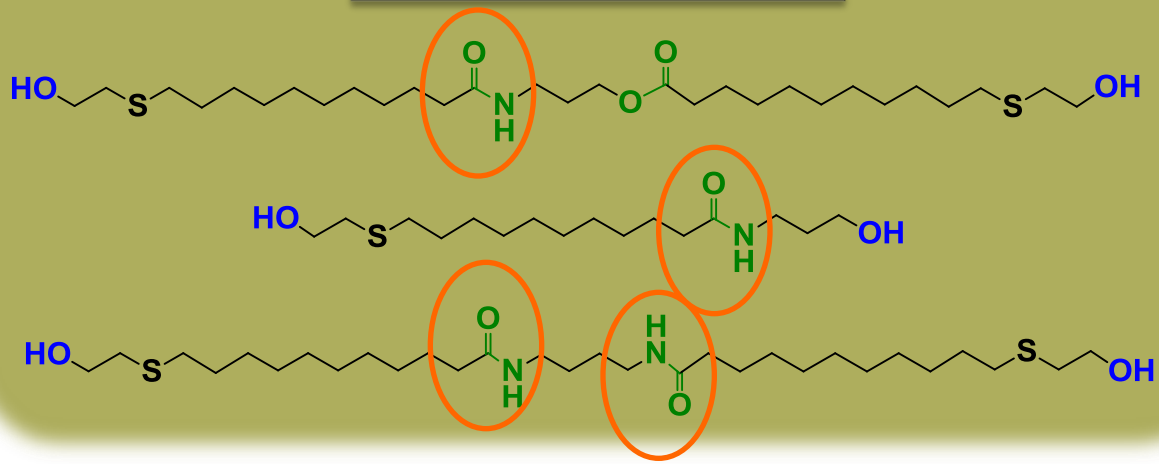
Bio-based well-defined difunctional building-blocks

Bio-based Thermoplastic polyesters & poly(ester-amide)s

Polyesters

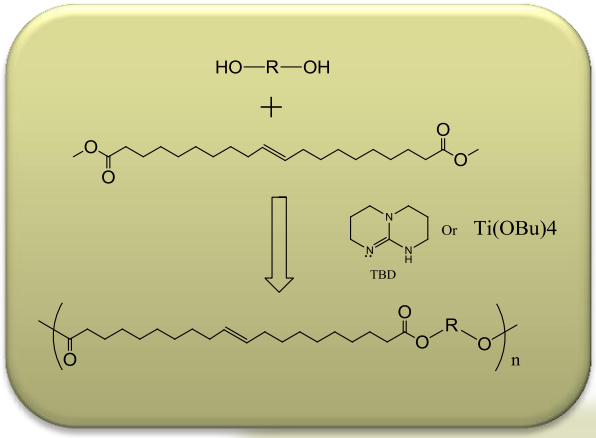


Poly(ester-amide)s

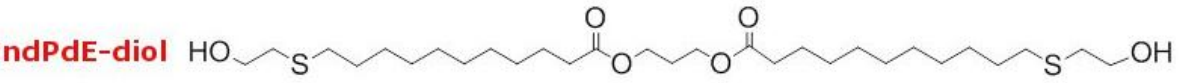


Polyesters using diol precursors

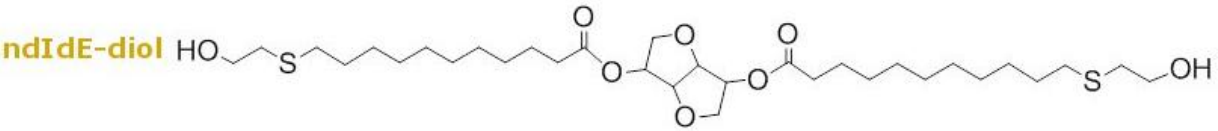
Fats & Oils expertise



UndPdE-diol



UndIdE-diol

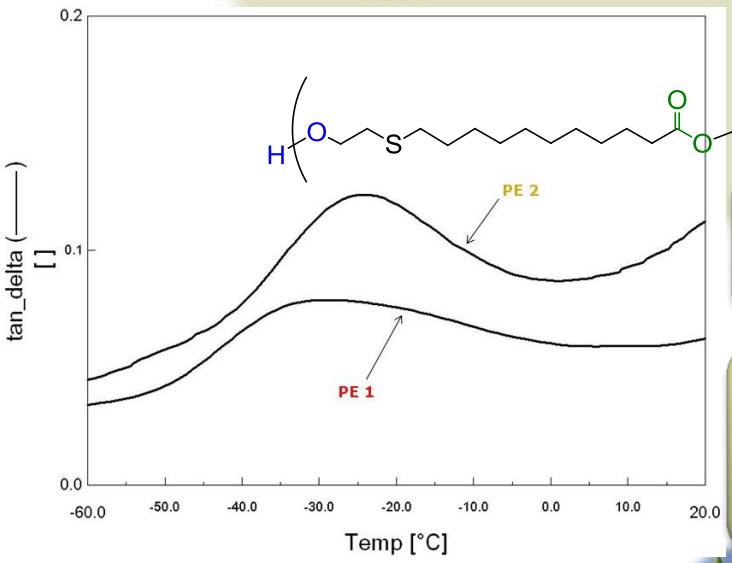


	Diol	ester:amide ratio	Mn (g/mol)	Mw (g/mol)	Mw/Mn
PE 1	UndPdE	1:0	18 400	35 000	1.9
PE 2	UndIdE	1:0	8 900	13 300	1.5

SEC in THF , PS calibration

Dynamic mechanical analysis (compression mode)

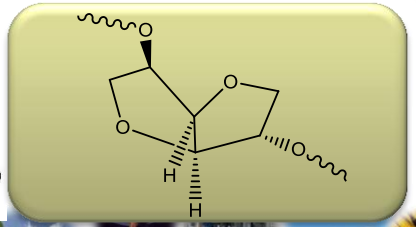
Tan δ



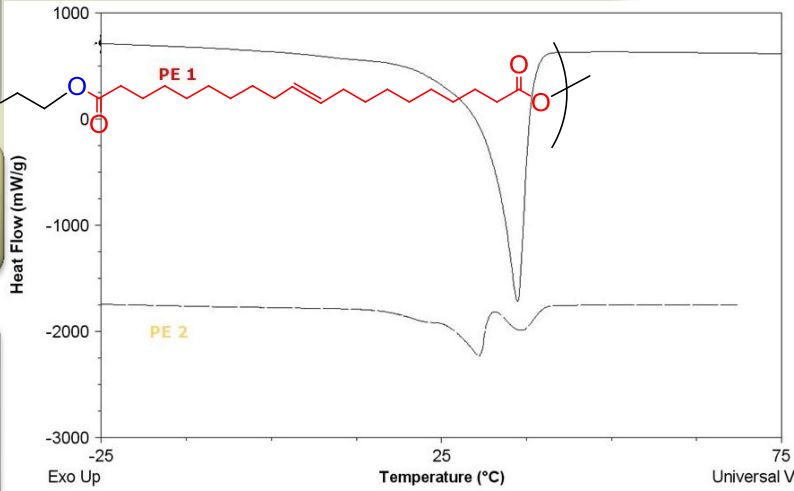
Storage Modulus : E'
Loss Modulus : E''

$$\tan\delta = \frac{E''}{E'}$$

Low increase of glass transition (10°C) with incorporation of Isosorbide



DSC – 10°C/min



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Our strategy to more robust fatty-acid based materials

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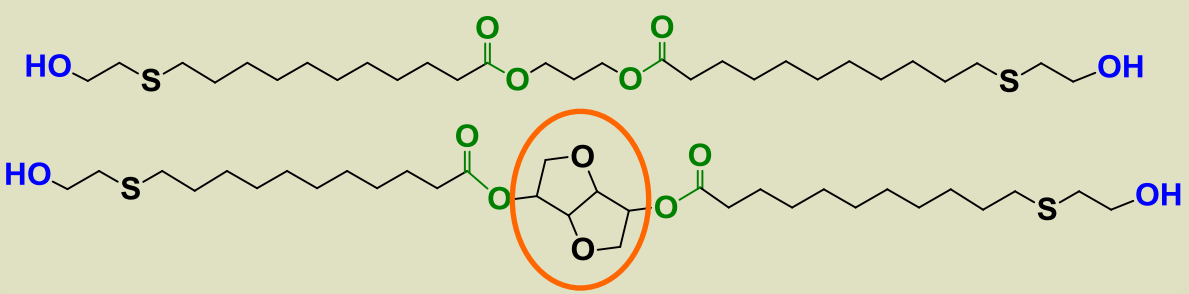
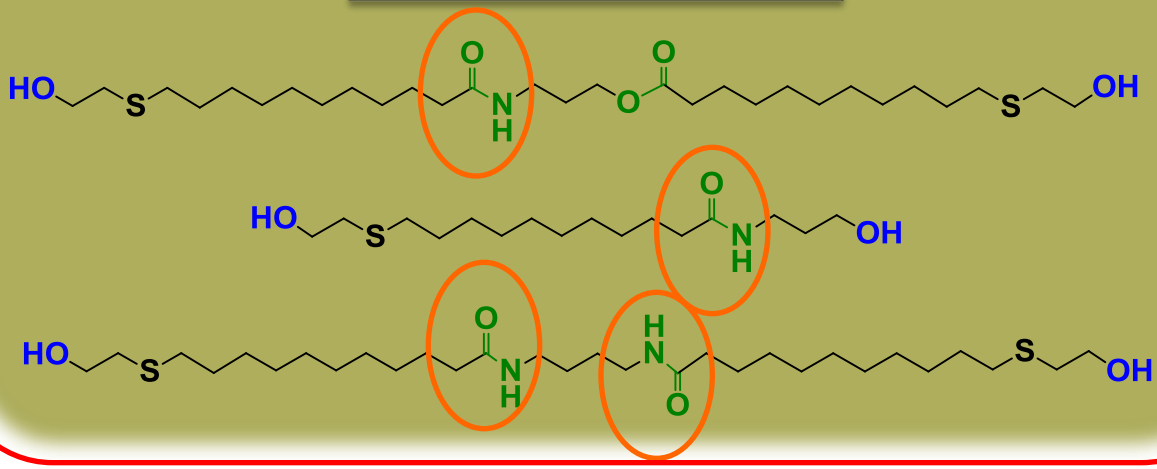
Bio-based well-defined difunctional building-blocks

Bio-based Thermoplastic polyesters & poly(ester-amide)s

Polyesters



Poly(ester-amide)s



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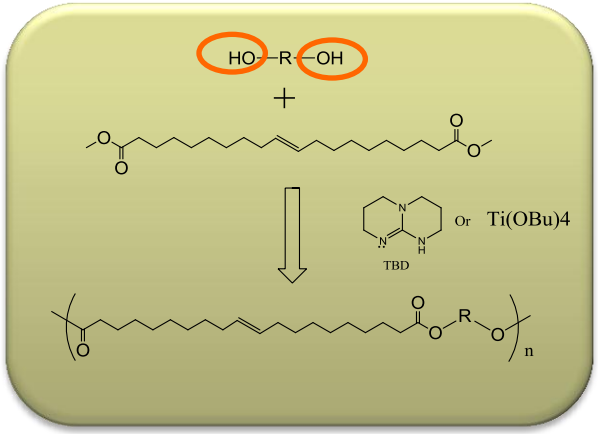
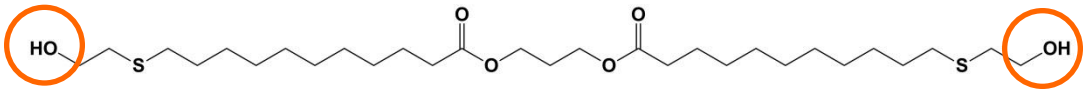
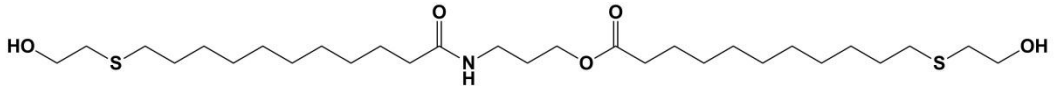
Poly(ester-amide)s : promising bio-based materials



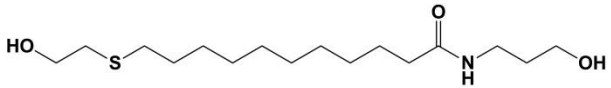
UndPdE-diol



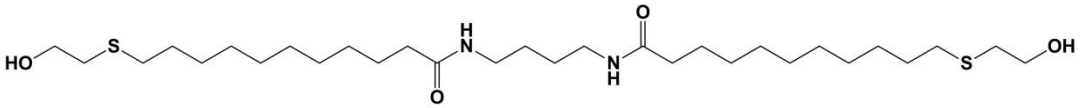
UndPEA-diol



UndPmA-diol

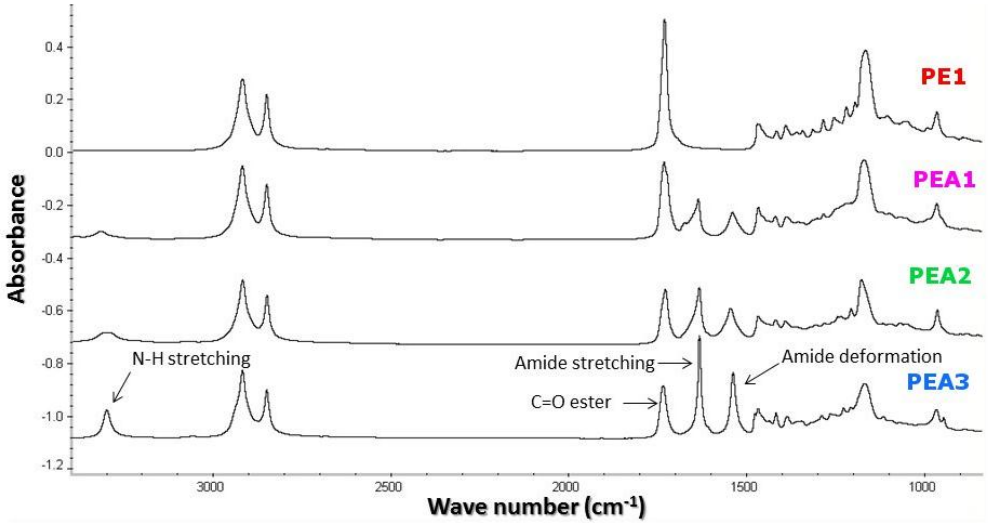


UndBdA-diol

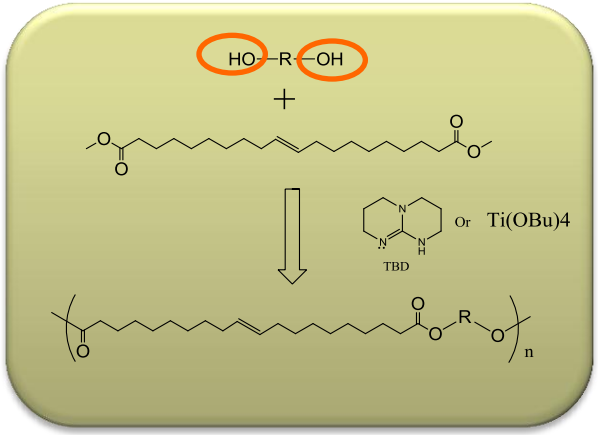


Entry	Monomer	ester:amide ratio	Mn (g/mol)	Mw (g/mol)	Mw/Mn
PE 1	UndPdE	1:0	18 400	35 000	1.9
PEA 1	UndPEA	3:1	17 500	33 100	1.9
PEA 2	UndPmA	2:1	10 902	19 500	1.8
PEA 3	UndBdA	1:1	19 300	29 000	1.5

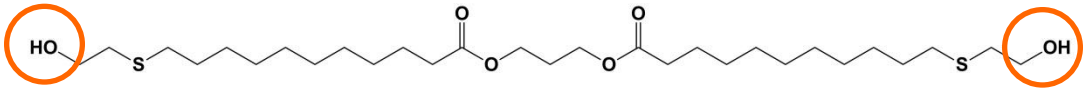
SEC in THF , PS calibration - For PEA3, trifluoroacetic anhydride was used to dissolve the polymer using standard method



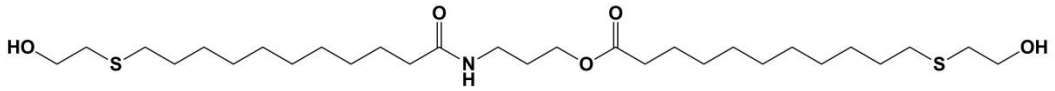
Poly(ester-amide)s : promising bio-based materials



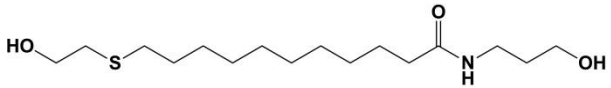
UndPdE-diol



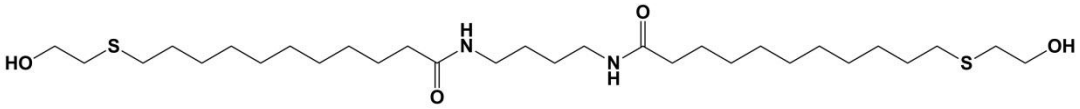
UndPEA-diol

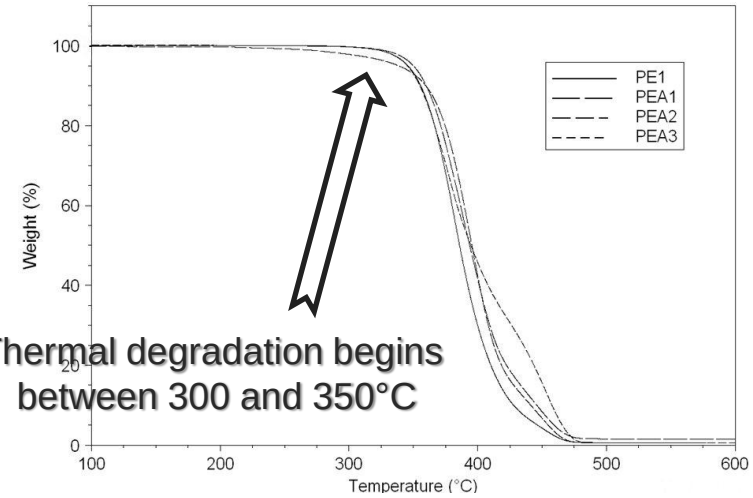


UndPmA-diol

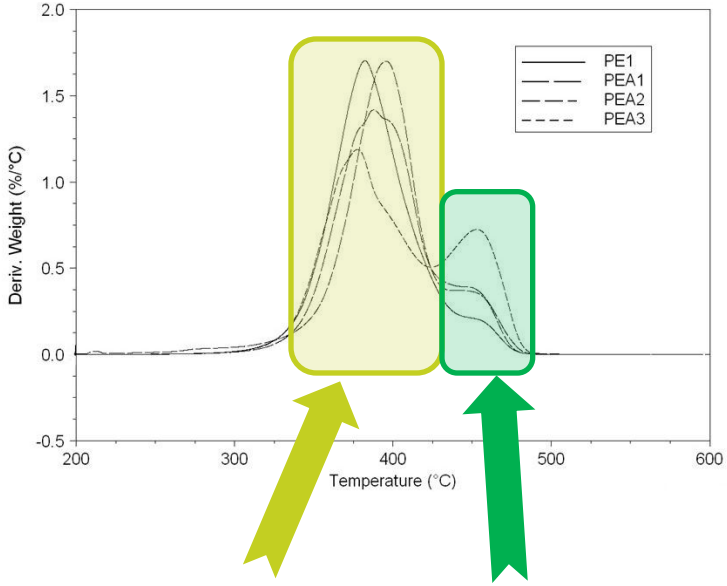


UndBdA-diol





TGA 10°C/min



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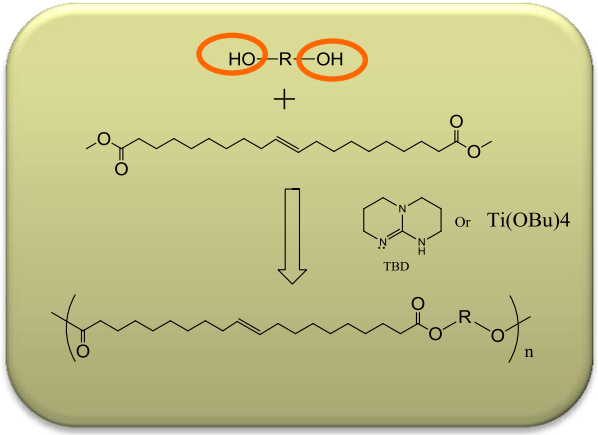
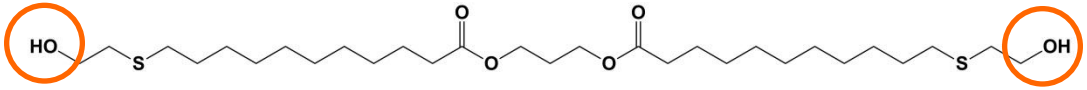
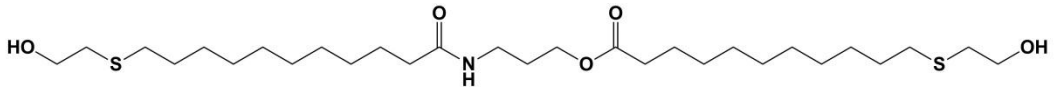
Poly(ester-amide)s : promising bio-based materials



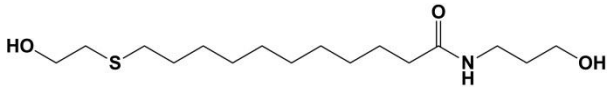
UndPdE-diol



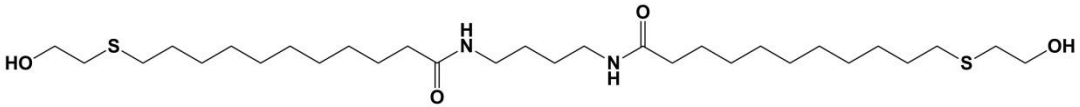
UndPEA-diol

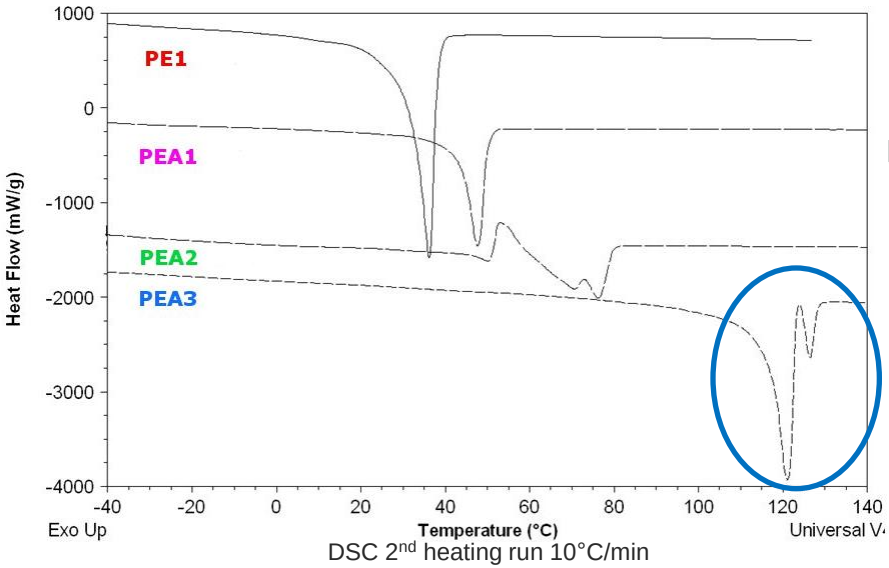


UndPmA-diol



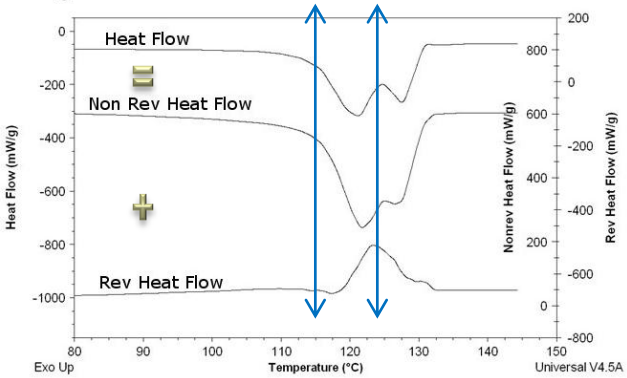
UndBdA-diol



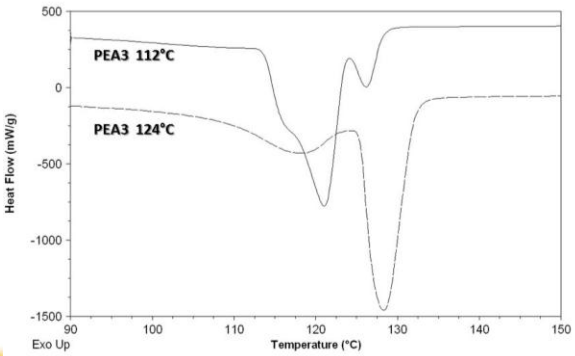


DSC 2nd heating run 10°C/min

Modulated DSC 2°C/min



30min Annealing 10°C/min



High increase of melting point with hydrogen bond density
36°C < Tm < 126°C

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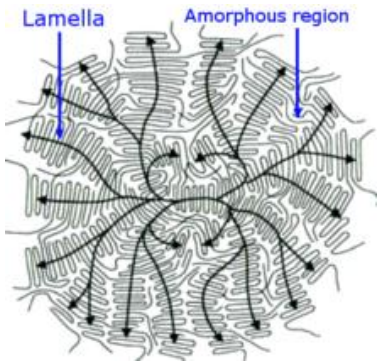
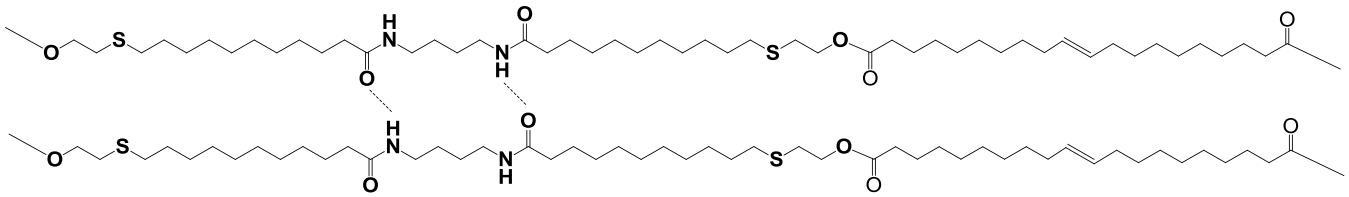


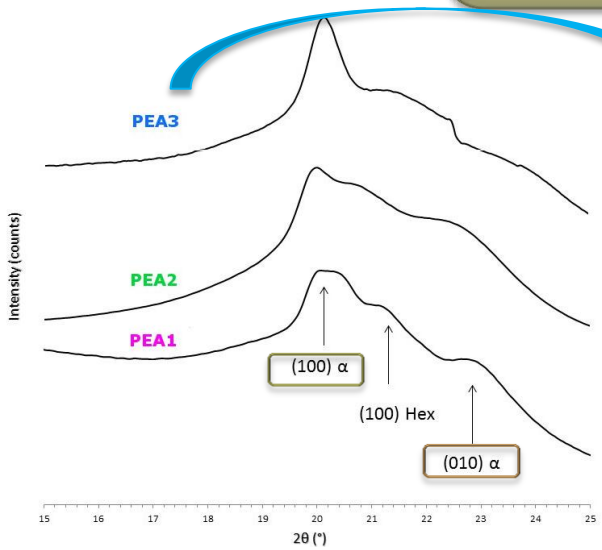


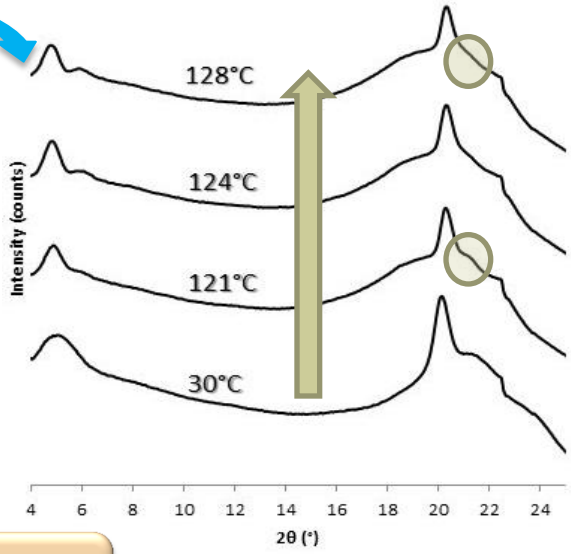
Chemical structure comparable to Nylon

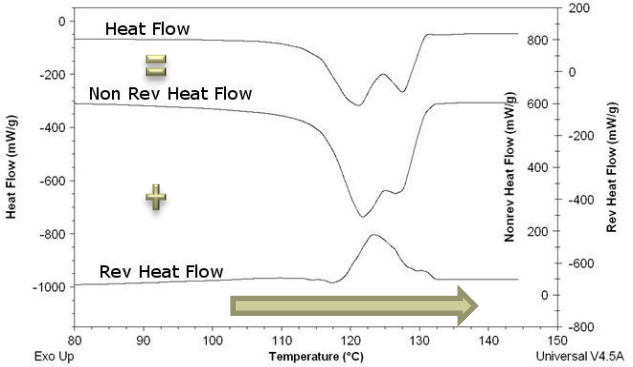
α form : hydrogen bonds between antiparallel chains

γ form : hydrogen bonds between parallel chains

Metastable pseudohexagonal structures which vary continuously in size, perfection, and structural parameters







amide-amide intermolecular H-bonded chains (~4.8 A)

van der Waals packed sheets (~3.7A)

Disappearance of pseudohexagonal reflection by heating

=

Melting of pseudohexagonal form which crystallize in the α-form

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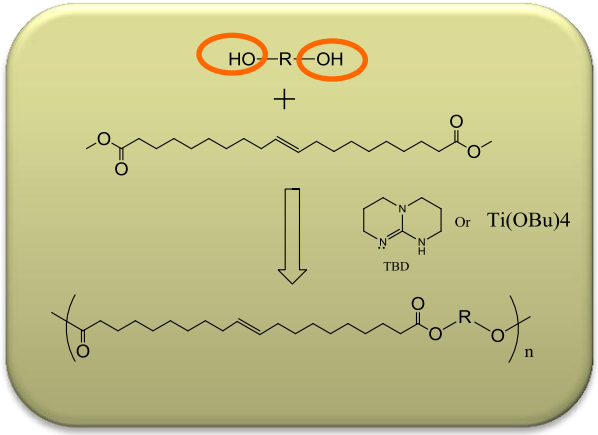
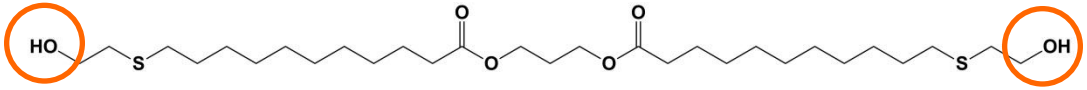
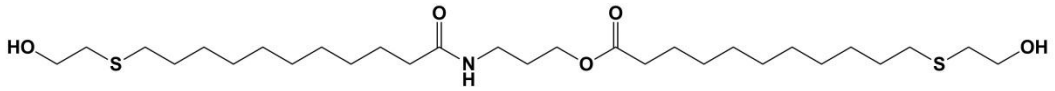
Poly(ester-amide)s : promising bio-based materials



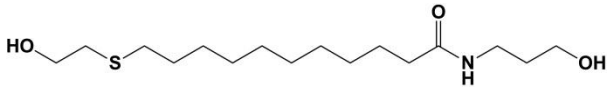
UndPdE-diol



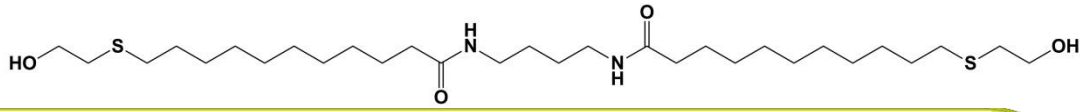
UndPEA-diol



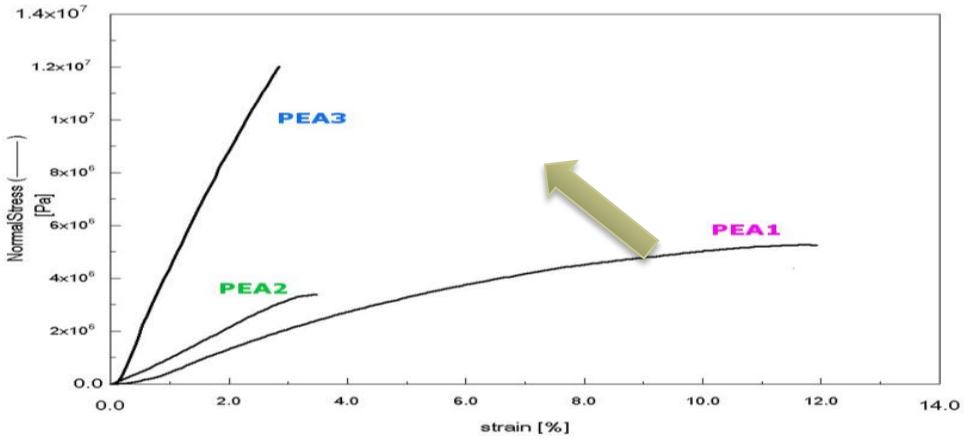
UndPmA-diol



UndBdA-diol



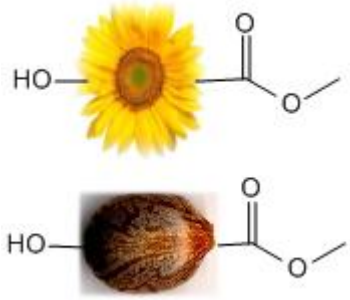
Tensile tests



Entry	Young's Modulus (MPa)	Ultimate Strength (MPa)	Strain at break (%)
PE1	93.0 ± 10.4	2.9 ± 0.8	4.1 ± 1.3
PEA1	82.7 ± 15.2	5.4 ± 1.2	11.1 ± 2.4
PEA2	131.5 ± 17.5	3.5 ± 0.3	3.4 ± 0.7
PEA3	363.0 ± 89.1	10.0 ± 3.5	3.3 ± 0.7

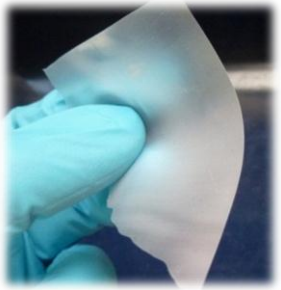
Conclusion

HYDROXYESTERS

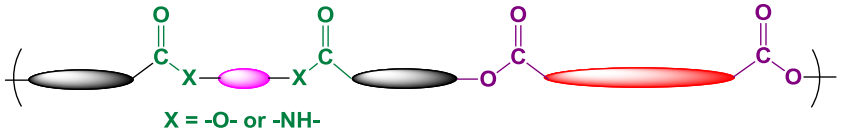


POLYESTERS

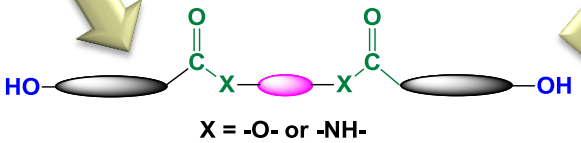
AB TYPE CONDENSATION



POLY(ESTER-AMIDE)S WITH IMPROVED THERMO-MECHANICAL PROPERTIES

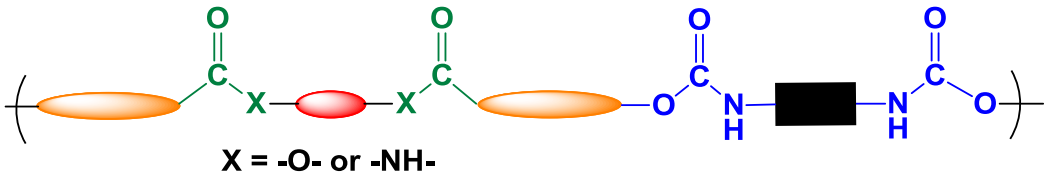


ESTER AND/OR AMIDE DIOL PRECURSORS



DIOL + DIESTER CONDENSATION

POLY(ESTER-AMIDE)S URETHANES WITH IMPROVED THERMO-MECHANICAL PROPERTIES



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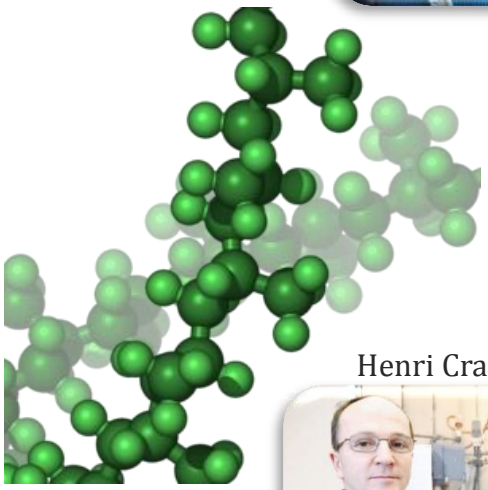
Acknowledgments

Lise Maisonneuve
PhD 2A

Thomas lebarbé
PhD 2A



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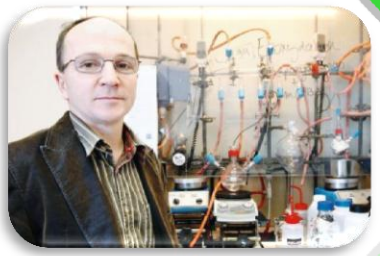
Henri Cramail



Benoit Gadenne

REGION AQUITAINE

ADEME
Agence de l'Environnement et de la Maîtrise de l'Energie